



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Life cycle assessment of advanced oxidation processes for olive mill wastewater treatment

Citation for published version:

Chatzisyseon, E, Foteinis, S, Mantzavinos, D & Tsoutsos, T 2013, 'Life cycle assessment of advanced oxidation processes for olive mill wastewater treatment', *Journal of Cleaner Production*, vol. 54, pp. 229-234. <https://doi.org/10.1016/j.jclepro.2013.05.013>

Digital Object Identifier (DOI):

[10.1016/j.jclepro.2013.05.013](https://doi.org/10.1016/j.jclepro.2013.05.013)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Early version, also known as pre-print

Published In:

Journal of Cleaner Production

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



REFERENCE: E. Chatzisyneon, S. Foteinis, D. Mantzavinos, T. Tsoutsos, Life cycle assessment of advanced oxidation processes for olive mill wastewaters treatment, *Journal of Cleaner Production* **54** (2013) 229-234. <http://dx.doi.org/10.1016/j.jclepro.2013.05.013>

Life Cycle Assessment of Advanced Oxidation Processes for Olive Mill Wastewater Treatment

Efthalia Chatzisyneon, Spyros Foteinis, Dionissios Mantzavinos, Theocharis Tsoutsos*

Department of Environmental Engineering, Technical University of Crete,
Polytechnioupolis, GR-73100 Chania, Greece.

*Corresponding author: E-mail: theocharis.tsoutsos@enveng.tuc.gr,

Tel.: 0030 2821037825

ABSTRACT

The efficient management of biorecalcitrant agro-industrial effluents, such as olive mill wastewater (OMW), is a matter of concern along all Mediterranean countries. However, the applicability of any treatment technique is strongly related, apart from its mineralization and detoxification efficiency, to its joint environmental impacts. In this work, the life cycle assessment methodology was utilized to estimate the environmental footprint of three advanced oxidation processes (AOPs), namely UV heterogeneous photocatalysis (UV/TiO₂), wet air oxidation (WAO) and electrochemical oxidation (EO) over boron-doped diamond electrodes, for OMW treatment. It was observed that both EO and WAO can be competitive processes in terms of COD, TPh and color removal. EO was found to be a more environmentally friendly technique as it yields lower total environmental impacts, including CO₂ emissions to atmosphere. The environmental impacts of all three AOPs show that human health is primarily affected followed by impacts onto resources depletion. All in all, it was found that the environmental sustainability of AOPs is strongly related to their energy requirements and that their total environmental impacts decline according to the following order: UV/TiO₂ > WAO > EO.

Keywords: LCA; olive mill wastewater; environmental impacts; photocatalysis; electrolysis; wet air oxidation

1. Introduction

The foodstuff processing industry based on olive oil extraction constitutes a large part of agro-industrial activities and is an economically important activity for many Mediterranean regions. However, this process results in seasonal large quantities of biorecalcitrant wastewaters, that come from the vegetation water and the soft tissues of the olive fruits mixed with the water used in the different stages of oil production. All these wastewaters together with the industry wash-waters, make up the so-called olive mill wastewaters (OMW). The main environmental impacts of OMW derive from its high organic (COD values range between 45 - 170 g/L) and polyphenolic content (0.5 - 24 g/L) that result in high ecotoxicity and strong antibacterial action (Chatzisyneon et al., 2009a and 2009b). The presence of these biorecalcitrant organic compounds together with the seasonal production of large OMW quantities (about $4 \cdot 10^5 \text{ m}^3/\text{y}$ in Greece) constitute the major obstacles in the efficient effluent management.

Up to now, the majority of agro-industrial effluents such as OMW were discharged to evaporation ponds where they are left to evaporate naturally with the most hazardous of all being the seepage of organic pollutants into groundwater (Avraamides and Fatta, 2008; Komnitsas et al., 2011; Salomone and Ioppolo, 2012). The direct discharge of OMW to evaporation ponds was prohibited by Greek legislation. Olive mills operation is regulated by the new Laws 3982/11 and 4014/11 that establish a classification of olive mills according to their capacity and their environmental impacts and define the environmental commitments of each activity (Hellenic Republic, 2011a and 2011b). These are further specified by the Joint Ministerial Decision 15/4187/266 (Hellenic Republic, 2012) where it is made clear to olive mill operators that OMW has to undergo pre-treatment in order to reach an organic load of about 1 g/L COD, thus it can be safely discharged to evaporation ponds or be reused after further treatment. Hence, researchers have been focused on the investigation of new treatment strategies that would efficiently treat OMW and safely discharge it to the environment.

1 A great variety of physical, chemical, thermal and biological processes, as well as
2 several combinations of them, have been investigated for OMW treatment aiming at
3 removing the organic matter from the liquid phase in order to make it acceptable for
4 discharge into the environment. Among them, advanced oxidation processes (AOPs)
5 have been extensively studied regarding their efficiency to treat OMW, while it is
6 generally accepted that a process train comprising aerobic/anaerobic biological and
7 advanced oxidation processes may be the only viable option to treat OMW
8 (Mantzavinos and Kalogerakis, 2005). Generally, research efforts have been mainly
9 directed towards the investigation of the operating conditions of AOPs that affect OMW
10 mineralization and/or detoxification (Chatzisyneon et al., 2009c; Mert et al., 2010),
11 while there are few studies comparing several processes, including AOPs, from the
12 economical point of view (Cañizares et al., 2009). However, when designing or
13 planning a new technology its environmental impacts should be taken into account,
14 which have not yet been identified for OMW treatment. Therefore, a comparison of
15 AOPs environmental impacts for agro-industrial effluents treatment is a highly
16 important subject that is still pending.

17 Regarding wastewater treatment, AOPs have been primarily proposed as a pre- or post-
18 treatment step to destruct the most bio-recalcitrant organic substances before or after
19 further biological or physicochemical treatment (Chatzisyneon et al., 2009b).
20 Comninellis et al. (2008) declared that the higher the polluting load and the extent of
21 pollution removal needed, the harsher the treatment conditions to be applied are. In this
22 view, OMW treatment performance can be enhanced only by coupling several of the
23 above processes including AOPs.

24 The goal and scope of this work is to utilize the life cycle assessment (LCA)
25 methodology in order to assess the environmental footprint of several AOPs in bench-
26 scale, under Greek conditions, to identify their advantages and disadvantages in terms
27 of their environmental impacts, compare them and provide feedback on the most
28 sustainable process for future scaling-up of the OMW treatment facilities. For this
29 purpose, three advantageous, regarding organics degradation efficiency, AOPs, for
30 wastewater treatment, namely UV heterogeneous photocatalysis (UV/TiO₂), wet air
31 oxidation (WAO) and electrochemical oxidation (EO) over boron-doped diamond
32 electrodes, were studied. However, the environmental footprint of each of these
33 techniques has to be taken into account to get a thorough picture of the whole problem.
34 Up to now and to the authors' best knowledge, there is no published research dealing

with this subject. Moreover, these techniques were compared in terms of organics degradation efficiency and energy requirements in order to assess their overall performance from both an environmental and technical point of view.

2. Materials and Methods

2.1 Description of the studied wastewater

The OMW was once collected by a three-phase olive oil mill company, located in Chania, Western Crete, Greece. The effluent was subjected to filtration to remove most of its total solids and it was then kept at 4°C, to ensure that its physicochemical characteristics will not be lessened or weathered. The effluent had a strong malodor of degraded olive oil, a dark black-brown color and its main properties prior to and after filtration are given in Table 1.

Table 1.

It has to be noted that OMW sample was diluted with distilled water to achieve the appropriate initial COD value as shown in Table 2.

2.2 Experimental runs

This work is based on previously published experimental studies used to derive optimal operating parameters for three common AOP systems, namely photocatalytic (UV/TiO₂), electrochemical and wet air oxidation. The main parts and characteristics of these systems are given at Table 2. More details regarding the experimental set-ups, their operating mode and conditions of the oxidation processes are given in Chatzisyneon et al. (2009a, 2009b and 2009c). To meet these operating standards (i.e. initial COD), AOPs should be utilized as part of a treatment battery incorporating various physicochemical and biological processes as can schematically be illustrated in Figure 1.

Figure 1.

Keeping in mind the potential use of these processes in train treatment schemes (Figure 1), it was decided to investigate whether the bench-scale experimental data obtained from our previous publications (a summary of which is shown in Table 2) can be used

to scale-up the process and further perform an LCA at larger scale. Therefore, a pre-design cost estimation of the three AOPs was performed for a prospective industrial AOP treatment plant for OMW treatment. Generally, direct scaling-up from laboratory to industrial scale bears serious calculating inaccuracies. Hence, performance of the AOPs technologies should take place at pilot-scale first, before any further larger-scale application. However, the proposed pre-designing cost methodology can be a useful tool for researchers to get an indicative view of treatment expenses when scaling-up such processes.

2.3 Impact assessment methodology

The software package SimaPro 7.3.3 (PRe Consultants, 2012) was used in this work and the mandatory (selection of impact categories, category indicators and characterization models, classification, and characterization) and optional (normalization, grouping, and weighting) elements of the life cycle impact assessment (LCIA) according to ISO 14040 were utilized (ISO 14040, 2006; Tsoutsos et al., 2010; Foteinis et al., 2011). Furthermore, two impact assessment methods were used and these are IPCC 2007 version 1.02 and ReCiPe version 1.06. The first one compares processes based on CO₂ emissions equivalent (CO₂-eq), used to measure global warming potential (GWP), which is a standard indicator of environmental relevance. The ReCiPe framework, which encompasses GWP indicator, is the most recent impact assessment method that exhibits certain advantages comparing to other approaches, such as Eco-Indicator 99. The primary advantage is that ReCiPe comprises a broadest set of midpoint impact categories, including several environmental issues, one of them being GWP, to assess sustainability (Goedkoop et al., 2009). Analytically, the ReCiPe method can transform the life cycle inventory (LCI) results into a limited number of indicator scores that are expressed per environmental impact category and also as an aggregated single score. Furthermore the results were simulated using the three different perspectives, namely individualist (I), hierarchist (H) and egalitarian (E). The latter was finally chosen to evaluate the results, since it takes into account the long term, precautionary environmental impacts, which better corresponds to the scope of this study.

2.3.1 System boundaries

First of all, the system boundaries for each AOP were determined (Figure 2). In this study, OMW generation and its transportation to the laboratory were not included inside

the boundaries, since AOPs can be applied as an onsite treatment nearby the olive mill. Finally, since this work refers to experiments that were carried out in laboratory-scale, land use was not taken into account. The main system flows of this work were: (i) the energy inputs (electricity provided from the local grid), (ii) the three laboratory units, (iii) the materials that were used (TiO₂, oxygen, etc.), and (iv) their outputs to nature. Another important factor that should be taken into consideration is the CO₂ formed during OMW treatment. These CO₂ emissions were left outside of the system boundaries of this work because: (i) partial oxidation primarily occurs as evidenced by the relatively moderate COD decrease (18 - 34%), therefore total oxidation reactions that emit CO₂ are very limited, and (ii) there are no data in the literature that one could use to measure accurately the extent of total oxidation reactions (i.e. CO₂ emissions) during OMW treatment by AOPs.

Figure 2.

2.3.2 Functional unit

Treatment of 1 L of OMW was taken as the functional unit and the three oxidation processes were compared according to their yield in removing the two main environmental indicators of OMW, namely COD and TPh. COD is the first indicator since OMW with values higher than 1 g/L cannot be safely discharged to evaporation ponds or be reused. Although TPh are part of the COD they are considered as the second indicator and are examined separately, since if they are left untreated they are gradually oxidized and/or polymerized rendering OMW highly toxic and biorecalcitrant (Chatzisyneon et al., 2009b). Hence, AOPs were compared according to their environmental impacts in removing 1 g of COD and 1 g of TPh per liter of treated OMW. Finally, AOPs were also compared according to their efficiency in removing both pollutants. It has to be noted that COD and TPh removal depended on both the initial physicochemical characteristics of OMW and the applied AOP. Each applied AOP required different treatment time, energy consumption and was applied for different effluent volumes, while COD and TPh removal fluctuated, as shown in Table 2. Therefore, laboratory results were normalized to appropriate functional units, namely the removal of 1 g of COD and 1 g of TPh per liter of treated OMW (Table 2).

2.3.3 LCI

The inventory of the three laboratory units is analytically shown in Table 2. Specifically, the UV/TiO₂ laboratory unit includes a 400 W high-pressure mercury lamp with a lifespan of 5,000 h, as well as TiO₂ and oxygen. WAO inventory includes an alloy C-276 high-pressure reactor with a life span of 20 years (Parr Instruments, USA) and EO inventory includes a DiaCell® (type 100) single-compartment electrolytic flow-cell manufactured by Adamant Technologies with a life span of 10 years. The aforementioned inventory was simulated using the Ecoinvent v2.2 database.

Table 2.

It should be noted that due to the generally high life span of the three laboratory units their embodied energy (associated with producing the AOP treatment systems) is lower compared to their operating energy requirements and, therefore, most impacts are attributed to their operating energy. Moreover, another issue that needs to be mentioned is that electricity in Greece is currently provided by lignite (54%), oil (11%) and natural gas (17%), while only 18% is provided by renewables (European Commission, 2012).

Regarding WAO treatment, electrical energy is consumed during air compression, effluent mechanical stirring and heating of the reactor. In the present study, it was assumed that energy is mainly consumed for reactor heating and, therefore, any other electrical power requirements were considered as negligible.

Finally, during previous studies of our group the operating parameters that significantly affected UV/TiO₂, WAO and EO efficiency were estimated by utilising a factorial design methodology to perform and interpret the results. Based on this methodology the optimal operating parameters that would bring the best process performance for the same OMW sample were estimated.

It was found that both EO and WAO can be competitive processes in terms of organics degradation efficiency. However, it should be mentioned that AOPs will be applied in combination with a suitable process (i.e. physical, biological, etc.) for an integrated OMW treatment. Hence, apart from the high degradation efficiency of the process, other important aspects including environmental impacts, should be taken into consideration in order to proceed and decide on the most suitable oxidation technique for OMW treatment. In respect of this, an LCA methodology was utilized to assess the environmental impacts of each process.

3. Results and Discussion

3.1. LCIA results

LCIA is shown in Figure 3 for egalitarian where one can see the main contributions to the three processes; it is evident that the contribution of energy consumption to the UV/TiO₂ process is higher than the other two.

Figure 3.

Moreover, the results in terms of GWP for a timeframe of 100 years for the removal of 1 g/L COD and 1 g/L TPh are shown in Figure 4.

Figure 4.

It is obvious that EO is the most environmentally friendly AOP both in terms of COD and TPh removal. Specifically for the removal of 1 g COD, EO releases only 0.16 kgCO₂eq per liter of treated OMW, while the respective value for WAO is 0.88 kgCO₂eq. Besides, the UV/TiO₂ process exhibits the highest CO₂eq emissions since it releases 5.2 kgCO₂eq per liter of treated OMW. Regarding TPh removal, the results are consistent with those of COD removal; EO is more sustainable than UV/TiO₂ and WAO, releasing 1.24 kgCO₂eq per liter of treated OMW. WAO and heterogeneous photocatalysis emit 3 and 14.63 kgCO₂eq per liter of treated OMW, respectively, showing that the latter exhibits an order of magnitude greater GWP than the other two AOPs. This is consistent with the results reported by Chong et al. (2012) who compared several AOPs, including UV/TiO₂, for decentralized wastewater treatment. They found that CO₂ releases to the atmosphere were higher for UV-based than other AOPs. GWP is strongly related to energy consumption as this is the main reason for increased CO₂ emissions worldwide (Forster et al., 2007). At this point it is worth noticing the fact that the GWP of the three oxidation processes is proportional to their energy consumption. Hence, the lower CO₂eq emissions during the EO treatment are primarily attributed to the fact that the energy requirements for EO are lower than those for WAO and UV/TiO₂ (Table 2). Hence, the examined AOPs environmental impacts, in terms of their GWP, decline in the order: UV/TiO₂ > WAO > EO, rendering EO a more sustainable and likely to be applied technology than the other two. Therefore, it is concluded that the environmental sustainability of AOPs is strongly related to the

energy requirements of these technologies. This statement is consistent with the results reported by other researchers (Munoz et al., 2005 and 2006; Vince et al., 2008; Chong et al., 2012; Kohler et al., 2012) who observed that AOPs are more energy-intensive than material-intensive processes and, consequently, the energy consumption is the stage that generates the main environmental impacts. In the aforementioned studies, energy consumption was found to carry the highest environmental burden for several water and wastewater treatment plants either at laboratory or larger scales.

The aforementioned findings regarding GWP were also confirmed when the results were interpreted utilizing the ReCiPe method. This was used to provide a more holistic impact assessment of the overall process including the severity of each environmental impact onto human health, ecosystem and resources. The ReCiPe method transforms the LCI results into a broadest number of impact categories including the GWP environmental impact. Moreover, the key advantage of the ReCiPe method lies within the fact that it takes into account the severity of each impact category to assess the environmental sustainability of the process. Hence, the single and aggregated environmental impacts during the AOPs treatment, based on the ReCiPe method, for 1 g COD and 1 g TPh removal per liter of treated OMW, are presented in Figures 5 and 6.

Figure 5.

Figure 6.

Concerning both COD and TPh removal, it is observed that human toxicity impact category yields a higher score for the UV/TiO₂ process (Figure 5) than the other two. All other impact categories are not affected, in relative terms when compared to human health, by the OMW treatment technique. Furthermore, WAO shows higher severity level for human toxicity impact category, although it is about 83% lower for COD and 79% lower for TPh removal than UV/TiO₂. Yet, its environmental impact on fossil depletion and climate change human health categories can be assumed as very low. Moreover, EO achieves lower environmental impacts in terms of human toxicity impact. For example, it is about 97% and 81% lower than UV/TiO₂ and WAO, respectively for the removal of 1 g COD per liter of treated OMW. Additionally, it is worth noticing that EO poses very low environmental impacts to the other impact categories (Figure 5). There is no doubt that the most significant environmental impact

during OMW treatment is human toxicity for all the considered processes. This is primarily associated with the energy consumed during AOPs. Electricity in Greece is predominantly (i.e. 82%) provided by lignite, oil and natural gas, while only 18% is provided by renewable energy sources (European Commission, 2012). This mixture enhances (i) the production of toxic and hazardous by-products released to atmosphere and the aquatic environment, and (ii) the accumulation of greenhouse gases, thus increasing the impact of toxicity to humans. The aggregated impact categories according to the ReCiPe methodology can be seen in Figure 6, where UV/TiO₂ has the highest score of environmental impacts onto human health, indicating the low environmental sustainability of a bench-scale UV/TiO₂ laboratory unit operating under Greek conditions, when this is compared with EO or WAO. The main reason for this is that the bench-scale UV/TiO₂ laboratory unit is energy-intensive and utilizes non-environmentally friendly materials (high-pressure mercury lamp). Therefore, a scale-up unit should focus in reducing its energy demand by utilizing alternative and renewable energy sources or even move towards the use of solar energy as an irradiation source. These would make photocatalytic process a highly competitive technique for OMW treatment. Figure 6 also shows that EO achieves lower environmental impacts onto human health than the other two while the other damage categories are less affected by this process, thus leaving a considerable environmentally friendly footprint during OMW treatment. Accordingly, EO is a more environmentally friendly oxidation process for OMW treatment, while WAO follows with its total environmental impacts being twice and four times as much, in terms of TPh and COD removal, respectively.

4. Conclusions

The ultimate goal of this work was to identify the key environmental hotspots of three AOPs using LCA in order to provide feedback to support the sustainable development of future AOP units for scaling-up. The main conclusions drawn from this work are summarized as follows:

- The environmental sustainability of AOPs is strongly related to the energy requirements of these technologies, thus an increase of the process energy consumption enhances the environmental impacts of the whole process. This is consistent with results obtained by other researchers (Munoz et al., 2005 and 2006; Vince et al., 2008; Chong et al., 2012; Kohler et al., 2012) as AOPs are energy-intensive techniques.

- AOPs environmental impacts, in terms of their GWP and total environmental impacts, decrease in the order: $UV/TiO_2 > WAO > EO$, rendering EO a more sustainable technology, which may be applied for OMW treatment.
- UV/TiO_2 process was found to yield higher score onto human health, fossil resources and the ecosystem on our bench-scale laboratory unit operating under Greek conditions. Therefore, future studies should deal with the identification of the environmental impacts of a scaled-up heterogeneous photocatalysis system with different energy mixtures and especially renewable energy. On the other hand, EO shows lower overall environmental impacts onto human health, thus it can be considered as a more viable and sustainable option to reduce the organic load of OMW than the other two processes.

Overall, this work provides decision makers with a feedback regarding the environmental impacts of various AOPs when applied at bench-scale. So far, the selection of treatment technologies for agro-industrial effluents has been based on technical, socioeconomic and political criteria. The need to improve sustainability of the wastewater management and introduce environmental criteria in the decision making process is inevitable. Hence, this feedback will be beneficial for a potentially OMW treatment system implemented at large scale.

5. References

- Avraamides, M., Fatta, D., 2008. Resource consumption and emissions from olive oil production: a LCI case study in Cyprus. *J. Clean. Prod.* 16(7), 809-821.
- Cañizares, P., Paz, R., Sáez, C., Rodrigo, M.A., 2009. Costs of the electrochemical oxidation of wastewaters: A comparison with ozonation and Fenton oxidation processes. *J. Environ. Manage.* 90(1), 410-420.
- Chatzisyneon, E., Xekoukoulotakis, N.P., Diamadopoulos, E., Katsaounis, A., Mantzavinos, D., 2009a. Boron-doped diamond anodic treatment of olive mill wastewaters: Statistical analysis, kinetic modeling and biodegradability. *Water Res.* 43(16), 3999-4009.
- Chatzisyneon, E., Xekoukoulotakis, N.P., Mantzavinos, D., 2009b. Determination of key operating conditions for the photocatalytic treatment of olive mill wastewaters. *Catal. Today* 144(1-2), 143-148.
- Chatzisyneon, E., Diamadopoulos, E., Mantzavinos, D., 2009c. Effect of key operating parameters during wet oxidation of olive mill wastewaters. *Water Sci. Technol.* 59(12), 2509-2518.
- Chong, M.N., Sharma, A.K., Burn, S., Saint, C.P., 2012. Feasibility study on the application of advanced oxidation technologies for decentralized wastewater treatment. *J. Clean. Prod.* 35(issue number missing), 230-238.
- Comninellis, C., Kapalka, A., Malato, S., Parsons, S.A., Poulios, I., Mantzavinos, D., 2008. Advanced oxidation processes for water treatment: advances and trends for R&D. *J. Chem. Technol. Biotechnol.* 83(6), 769-776.
- European Commission, 2012. EU energy in figures, http://ec.europa.eu/energy/publications/doc/2012_energy_figures.pdf, accessed on August 2012
- Forster, P., Ramaswamy, V., Artaxo, P., Bernsten, T., Betts, R., Fahey, D.W., Haywood, J., Lean, J., Lowe, D.C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz M., Van Dorland, R., 2007. Changes in atmospheric constituents and in radiative forcing. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

1 Foteinis, S., Kouloumpis, V., Tsoutsos, T., 2011. Life cycle analysis for bioethanol
2 production from sugar beet crops in Greece. *Energ. Policy* 39(9), 4834-4841.

3 Goedkoop, M., Heijungs, R., Huijbregts, M., Schryver, A., Struijs, J., Zelm, R., 2009.
4 ReCiPe 2008, A life cycle impact assessment method which comprises harmonised
5 category indicators at the midpoint and the endpoint level, First edition, Report I:
6 Characterisation. Ministerie van Volkshuisvesting, Ruimtelijke Ordening en
7 Milieubeheer.

8 Hellenic Republic, 2011a. Act 3982/11, Government Gazette, Bulletin 143A/17-06-2011.
9 Hellenic Republic, 2011b. Act 4014/11, Government Gazette, Bulletin 209A/21-09-2011.
10 Hellenic Republic, 2012. Joint Ministerial Decision 15/4187/266, Government Gazette,
11 Bulletin B1275.

12 ISO 14040, 2006. Environmental management – Life cycle assessment – Principles and
13 framework, International Organisation for Standardisation (ISO), Geneve.

14 Kohler, C., Venditti, S., Igos, E., Klepiszewski, K., Benetto, E., Cornelissen, A., 2012.
15 Elimination of pharmaceutical residues in biologically pre-treated hospital wastewater
16 using advanced UV irradiation technology: A comparative assessment, *J. Haz. Mat.*
17 Article in Press, DOI: 10.1016/j.jhazmat.2012.06.006.

18 Komnitsas, K., Zaharaki, D., Doula, M., Kavvadias, V., 2011. Origin of recalcitrant
19 heavy metals present in olive mill wastewater evaporation ponds and nearby agricultural
20 soils. *Environ. Forensics* 12(4), 319-326.

21 Mantzavinos, D., Kalogerakis, N., 2005. Treatment of olive mill effluents: Part I.
22 Organic matter degradation by chemical and biological processes – an overview.
23 *Environm. Internat.* 31(2), 289-295.

24 Mert, B.K., Yonar, T., Kiliç, M.Y., Kestioğlu, K., 2010. Pre-treatment studies on olive
25 oil mill effluent using physicochemical, Fenton and Fenton-like oxidations processes. *J.*
26 *Haz. Mat.* 174(1-3), 122-128.

27 Munoz, I., Rieradevall, J., Torrades, F., Peral, J., Domenech, X., 2006. Environmental
28 assessment of different advanced oxidation processes applied to a bleaching Kraft mill
29 effluent. *Chemosphere* 62(1), 9-16.

30 Munoz, I., Rieradevall, J., Torrades, F., Peral, J., Domenech, X., 2005. Environmental
31 assessment of different solar driven advanced oxidation processes. *Sol. Energy* 79(4),
32 369-375.

33 PRé Consultants., 2012. SimaPro 7, Life-Cycle Assessment software package, version
34 7.3.3. Printerweg 18, 3821 AD Amersfoort, The Netherlands.

- 1 Salomone, R., Ioppolo, G., 2012. Environmental impacts of olive oil production: a Life
- 2 Cycle Assessment case study in the province of Messina (Sicily). J. Clean. Prod.
- 3 28(issue number is missing), 88-100.
- 4 Tsoutsos, T., Kouloumpis, V., Zafiris, T., Foteinis, S., 2010. Life cycle assessment for
- 5 biodiesel production under Greek climate conditions. J. Clean. Prod. 18(4), 328-335.
- 6 Vince, F., Aoustin, E., Breant, P., Marechal, F., 2008. LCA tool for the environmental
- 7 evaluation of potable water production. Desalination 220(1-3), 37-56.
- 8

1 **List of Tables**

2

3 Table 1. Properties of OMW used in this study.

4

5 Table 2. Life cycle inventory and organics degradation efficiency for the three AOPs at
6 optimal operating parameters.

7

8

9

1 Table 1.

Physicochemical characteristics	OMW before filtration	OMW after filtration
COD, g/L	47	40
Total phenols (TPh), g/L	8.1	3.5
Total solids, g/L	50.3	0.6
pH	4.6	4.4
Conductivity, mS/cm	17	18

2
3
4

Table 2.

	AOP		
	UV/TiO₂	WAO	EO
<i>Experimental set-up configuration</i>			
Reactor type	Immersion-well	high-pressure reactor (Parr Instruments, USA)	DiaCell® (type100)
Reactor material	Borosilicate glass	Alloy C-276	Boron-doped diamond on silicon
Reactor inputs	UVA-400 W high pressure mercury lamp (Osram, HQL, MBF-U)	25 kg Alloy C-276 2.5 kg Polypropylene	0.26 g Diamond 0.1 g Boron 0.15 kg Silicon 1.6 kg Steel 0.7 kg Polypropylene
<i>Operating parameters</i>			
Treatment Time, h	4	1	7
COD initial, g/L	5.1	8.1	10
OMW volume, L	0.35	0.35	10
[TiO ₂ -P ₂₅], g/L	2	-	-
Charge passed, mA/cm ²	-	-	286
Temperature, °C	27	180	27
Pressure, atm	1	24.7	1
<i>Organics removal yield</i>			
COD removal (%)	18	34	28
TPh removal (%)	63	94	40
Decolorization (%)	66	74	33
<i>Energy requirements</i>			
Energy from the Greek grid	Lignite (54%), Oil (11%), Natural gas (17%), Renewable sources (18%)		
kWh for 1 g COD per L OMW removed	5	0.8	0.15
kWh for 1 g TPh per L OMW removed	14.2	2.9	1.2

List of Figures

Figure 1. Simplified scheme of the train treatment techniques for OMW treatment.

Figure 2. System boundaries of this work. (a) EO; (b) UV/TiO₂; (c) WAO

Figure 3. Dendrogram of the processes and their main contributions to environmental impacts for the removal of 1 g/L COD.

Figure 4. Global warming potential (GWP) in CO₂ equivalents for a timeframe of 100 years for the removal of 1 g/L COD and 1 g/L TPh for the three oxidation processes.

Figure 5. Severity of impact categories according to the ReCiPe methodology for the removal of 1 g/L COD and 1 g/L TPh, for the three oxidation processes.

Figure 6. Severity of aggregated damage categories according to the ReCiPe methodology for the removal of 1 g/L COD and 1 g/L TPh, for the three oxidation processes.

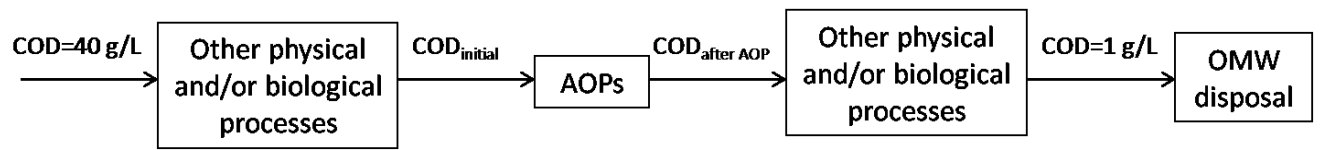


Figure 1.

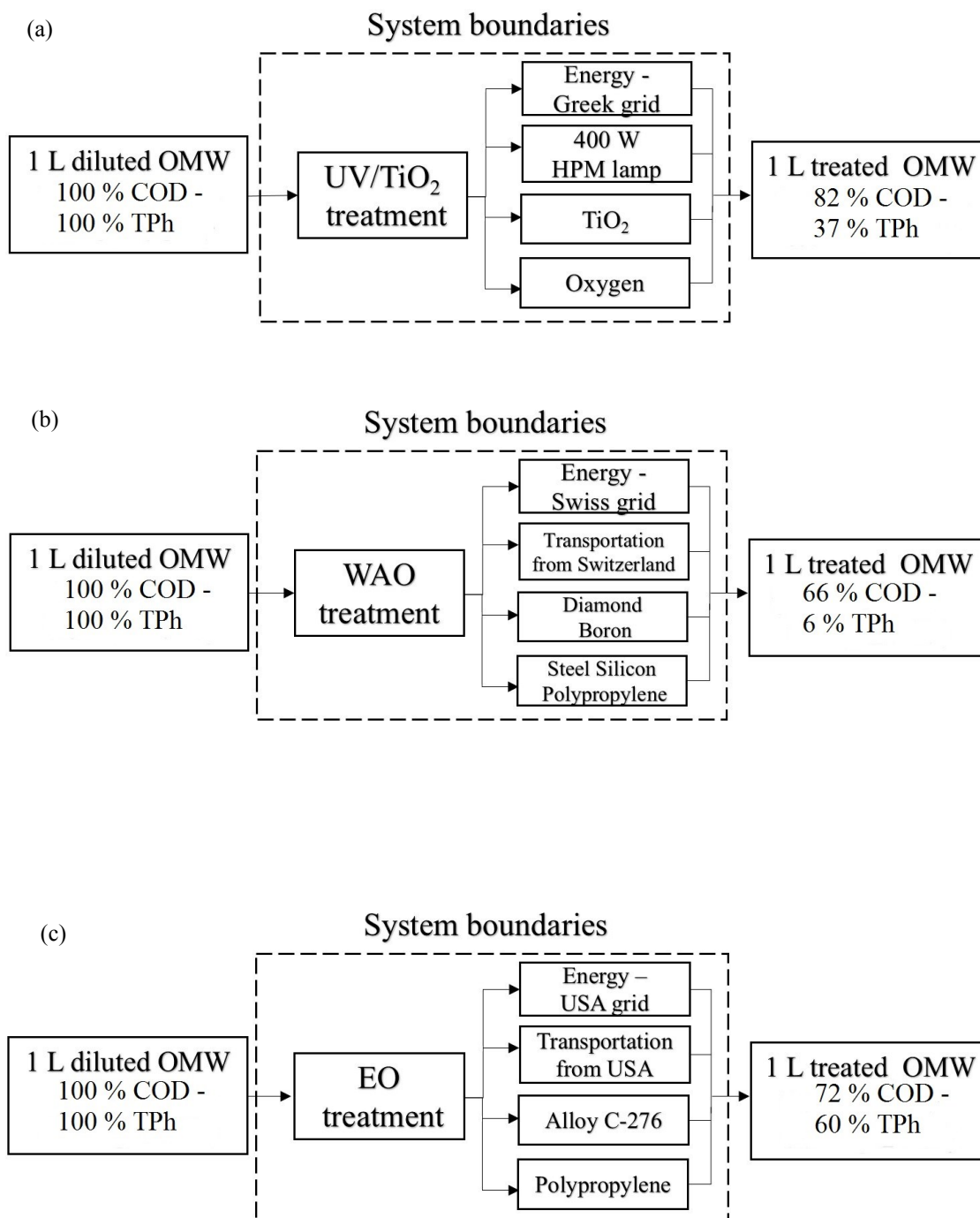


Figure 2.

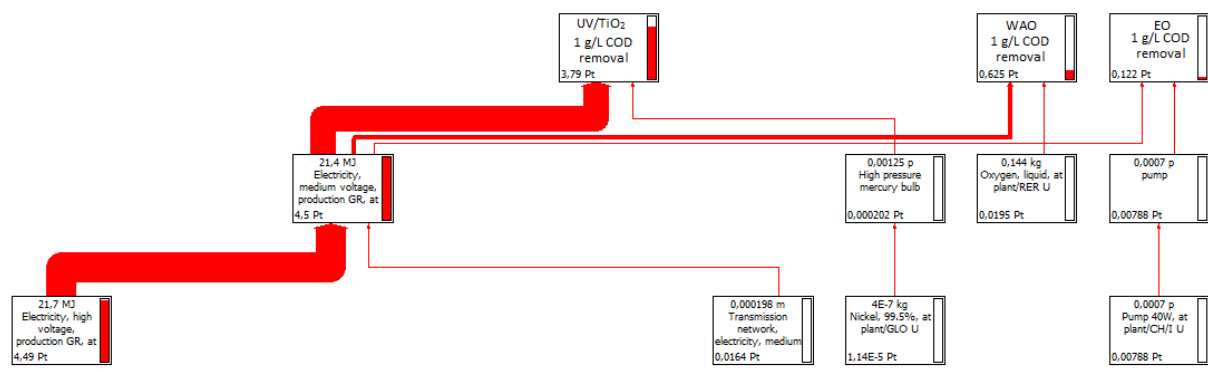
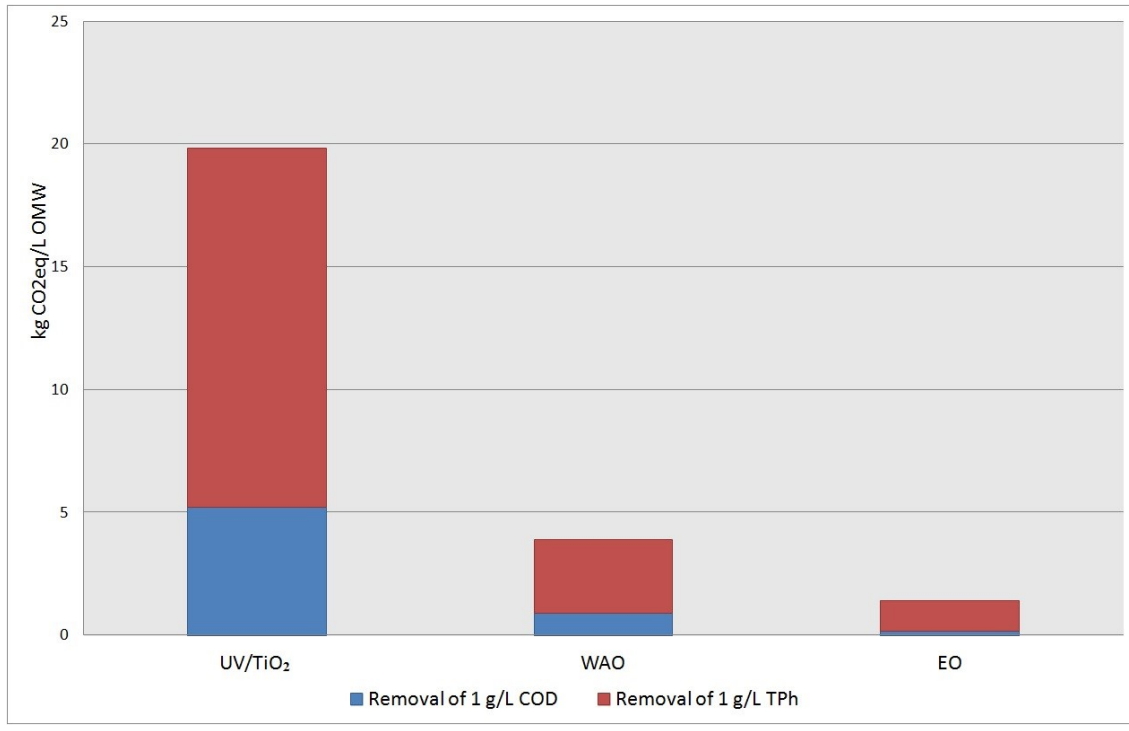


Figure 3.

1

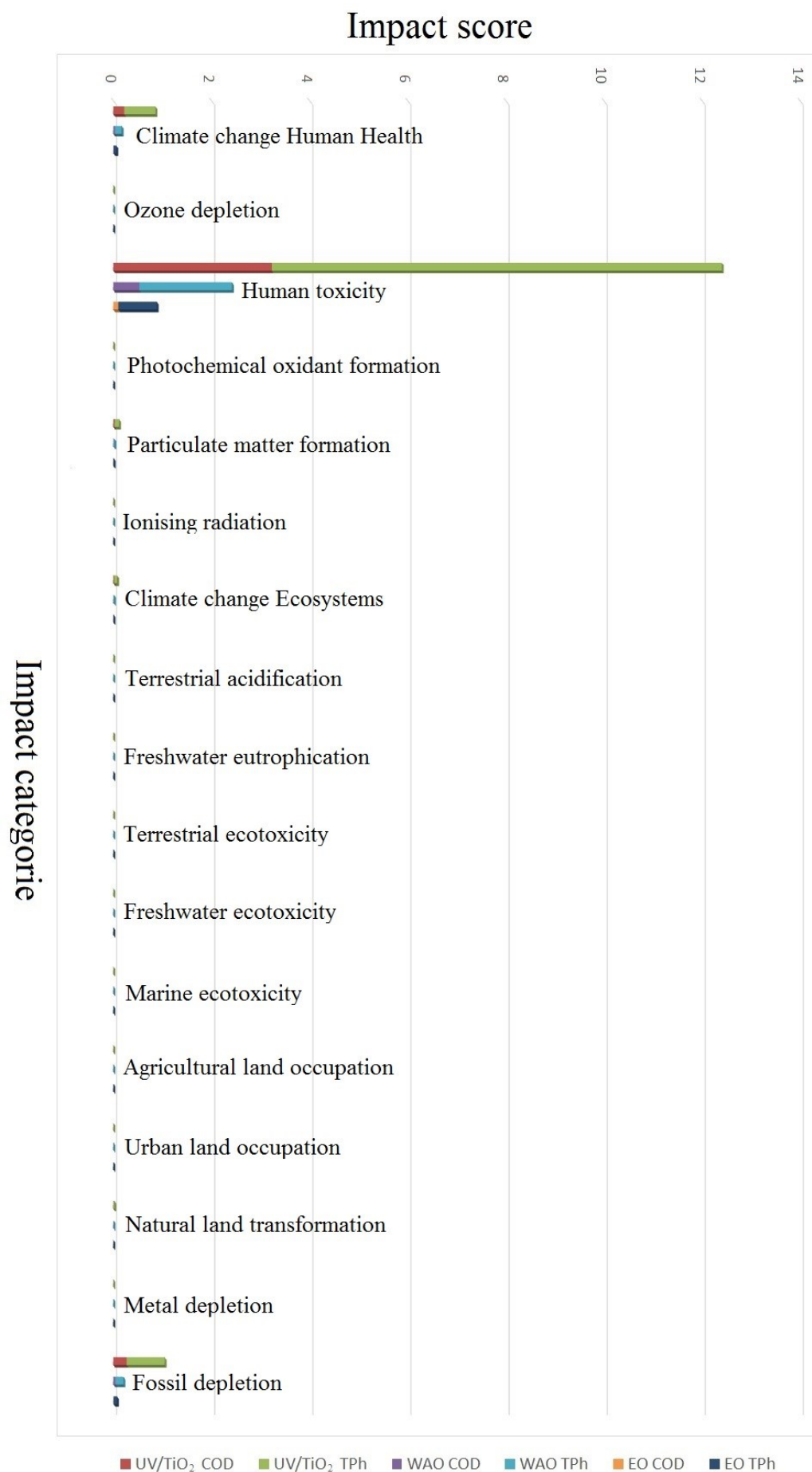


2

3

Figure 4.

4



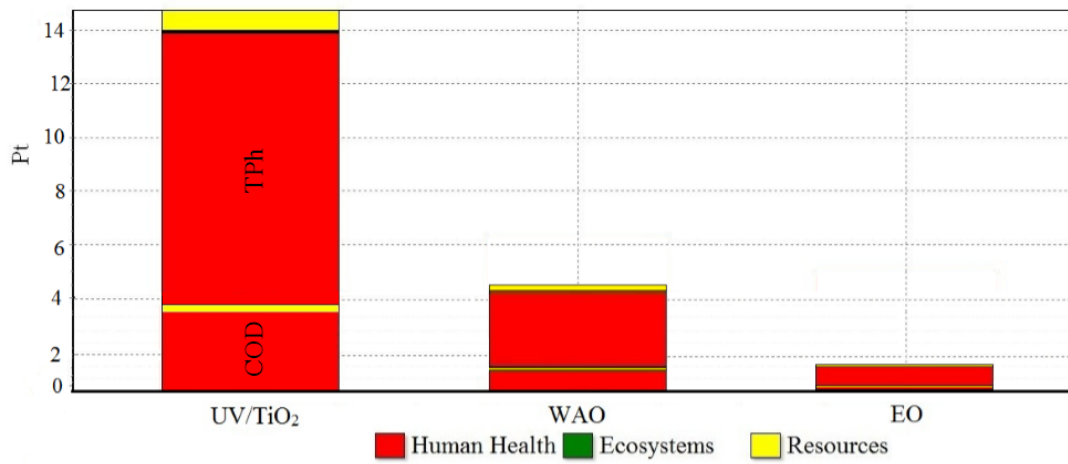
1 Figure 5.

2

3

4

5



6

7

8 Figure 6.